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Crystal Field Surface Orbital–Bond Energy Bond Order (CFSO-BEBO) Calculations for Surface Reactions

I. The Reactions $CO + O_2$, $NO + CO$ and $H_2 + O_2$ on a Platinum (111) Surface

W. H. WEINBERG

Division of Chemistry and Chemical Engineering,
California Institute of Technology, Pasadena, California 91109

AND

R. P. MERRILL

Department of Chemical Engineering,
University of California, Berkeley, California 94720

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The crystal field surface orbital–bond energy bond order (CFSO-BEBO) model of chemisorption has been extended in order to make predictions of activation energies of surface reactions. The reactions of O_2 with CO, NO with CO, and H_2 with O_2 on a Pt (111) surface are considered. The model allows a choice to be made between the Langmuir–Hinshelwood and Rideal–Eley mechanisms of surface reactions based on calculated activation energies. For each of the three reactions investigated the Rideal–Eley mechanism has the lowest activation energy. The H_2 and O_2 reaction is predicted to have zero activation energy, and the O_2 and CO reaction is predicted to have an activation energy of 16 kcal/mole. The reaction of NO and CO is predicted to proceed in the following way: The NO dissociates on the Pt surface with an activation energy of 12 kcal/mole, and the adsorbed O atom reacts with a gas phase CO molecule with an activation energy of 16 kcal/mole. The direct interaction of a gas phase CO molecule with an adsorbed NO *molecule* is predicted to have an activation energy of 37 kcal/mole, and this mechanism can thus be ruled out. Favorable comparisons are made between the model predictions and available experimental data.

INTRODUCTION

Recently an empirical model of chemisorption has been formulated which combines the crystal field concepts of transition metal chemistry and the bond energy-bond order relationships of gas phase spectroscopy (*1–4*). This model has been termed the crystal field surface orbital-bond energy bond order (CFSO-BEBO) model of chemisorption.

The CFSO model of a metal surface has been applied to face-centered cubic metal surfaces by Bond (*5,6*) drawing on previous ideas traditionally used in solid state chemistry (*7–10*). The 12 nearest neighbors and six next-nearest neighbors in a face-centered cubic metal are disposed in an octahedral environment as shown in Fig. 1. The *d*-orbitals in such a configuration split into two separate groups with one group pointing toward the next-nearest neighbors. The former group is known as the t_{2g} *d*-orbitals and are composed of the d_{xy}, d_{yz} and d_{zx} orbitals; while the latter group is known as the e_g *d*-orbitals and are composed of the $d_{x^2-y^2}$ and d_{z^2} orbitals. A pictorial description of the (111) plane of a face-centered cubic metal surface is shown in Fig. 2. As shown in Fig. 2, there are two different types of bonding sites on the

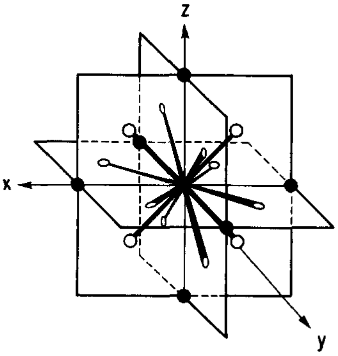

FIG. 1. The disposition of atoms about a central atom in a face-centered cubic metal. Near-neighbors (open circles) are bonded by overlap of t_{2g} orbitals and next-nearest neighbors (filled circles) by overlap of e_g orbitals after Bond (*5*).

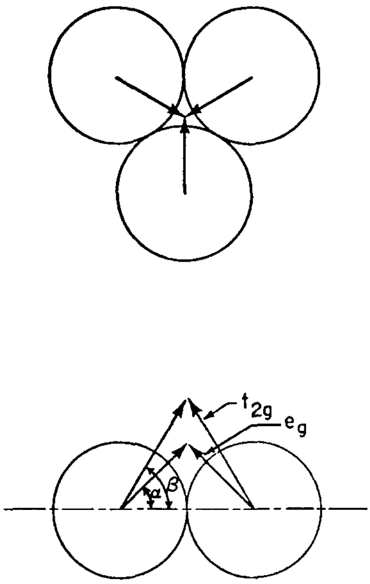

FIG. 3(top). Bonding site on the Pt (111) surface. The t_{2g} orbitals make an angle of 54°44′ with respect to the (111) plane and the e_g orbitals make an angle of 35°16′. (bottom) Side view of two of the three orbitals of (top) after a rotation of the (111) plane. $\alpha = \pi/4$ and $\beta = \pi/3$.

(111) plane. Half of the sites are composed of triads of t_{2g} orbitals which emerge at an angle of 54°44′ to the (111) plane, and the other half of the sites are composed of triads of e_g orbitals which emerge at an angle of 35°16′ to the (111) plane; both of the sets of sites possess threefold symmetry. The geometry of the two different types of adsorption sites is shown more explicitly in Fig. 3. The t_{2g} sites contain only the *d*-electrons mentioned above, whereas the e_g sites contain both *d*- and *p*-electrons. The maximum total number of metal electrons available at the t_{2g} sites before spin unpairing of the metallic electrons must be included is 1.80, and the maximum total number of unpaired electrons at the e_g sites is 3.80 (*1–3*). This picture of the electronic structure of the platinum surface is naive, to say the least. Even within the framework of a surface molecule concept, there is no reason not to expect, for example, some hybridization of the t_{2g} orbitals with *p*-orbitals. It is a zeroth order model, but it has been remarkably successful with these empirical model calculations (*1–4*) and is adopted here.

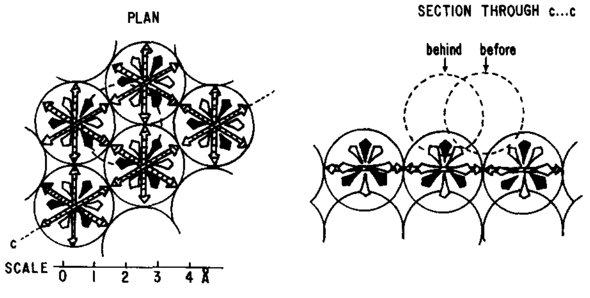

FIG. 2. Diagrammatic representation of the emergence of orbitals at the (111) face of a face-centered cubic metal. Filled arrows: e_g orbitals emerging at an angle of 35°16′ to the plane of the paper. Open arrows: t_{2g} orbitals emerging at an angle of 54°44′ to the plane of the paper. Cross-hatched arrows: bonding metal orbitals in the plane of the surface after Bond (*5*).

The CFSO-BEBO model has previously been applied to the chemisorption of hydrogen on (111) platinum (*1*); to the chemisorption of carbon monoxide, oxygen, and carbon dioxide on (111) platinum and oxygen on (111) nickel (*2*); to the chemisorption of nitrogen, nitrous oxide and nitric oxide on (111) platinum and nitrous oxide on (111) nickel (*3*); and to the chemisorption of oxygen on both clean and carbon contaminated platinum surfaces (*4*). Further details of the model may be found in these papers. In the present paper, the model is used to describe several heterogeneously catalyzed reactions (the oxidation of carbon monoxide by both oxygen and nitric oxide, and the reaction of hydrogen and oxygen to form water) on a (111) platinum surface. In order to apply the bond energy–bond order (BEBO) aspects of the model, it is necessary to know the way in which the pertinent bond energies vary as a function of bond order. This correlation from gas phase spectroscopy is shown in Fig. 4 for the bond between carbon and oxygen, and that between nitrogen and oxygen atoms (*11*).

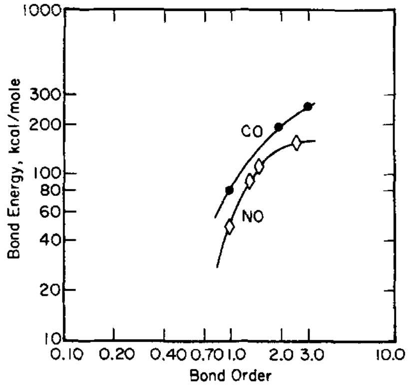

FIG. 4. Correlation between bond energy and bond order for CO (●), and NO (◇) bonds.

RESULTS AND DISCUSSION

Oxidation of Carbon Monoxide on Platinum (111)

Rideal–Eley Mechanism

It is known that the heat of adsorption of oxygen on platinum (111) is greater in magnitude than the heat of adsorption of carbon monoxide on that same surface. The CFSO-BEBO model has been used to show that the heat of adsorption of oxygen (dissociatively chemisorbed at two e_g sites) is approximately 68 kcal/mole, while the heat of adsorption of carbon monoxide (molecularly chemisorbed at an e_g site) is approximately 28 kcal/mole in agreement with experimental data (*2*). From a thermodynamic viewpoint then it is expected that oxygen adsorbs preferentially over carbon monoxide on the platinum surface or will replace adsorbed carbon monoxide unless the replacement is kinetically limited. When describing the oxidation of carbon monoxide in terms of a Rideal–Eley mechanism (i.e., one reactant adsorbed on the surface and the other reactant in the gas phase), it is assumed the oxygen is adsorbed atomically on the platinum (111) surface and the carbon monoxide impinges on the surface from the gas phase, viz,

$$\mathrm{Pt}=\mathrm{O}(e_g\ \text{site})+\mathrm{C}\equiv\mathrm{O(g)}\longrightarrow \mathrm{Pt}+\mathrm{O}=\mathrm{C}=\mathrm{O(g)}. \quad (1)$$

If symmetric electron transfer is assumed from the platinum–oxygen bond both to the carbon–oxygen bond being formed and back to the metal free valence, and simultaneous electron transfer from the carbon–oxygen bond in carbon monoxide to the carbon–oxygen bond being formed, then the appropriate bond conservation relations are given by

$$\begin{aligned} n_{\mathrm{Pt-O}} &= 2 - n_{\mathrm{O-CO}}, \\ n_{\mathrm{CO}} &= 3 - 0.5\, n_{\mathrm{O-CO}}, \\ n_{\mathrm{Pt-Pt}} &= 0.5\, n_{\mathrm{O-CO}}, \end{aligned} \quad (2)$$

where $0 \leqslant n_{\mathrm{O-CO}} \leqslant 2$. In Eq. (2) $n_{\mathrm{Pt-O}}$ is the order of the platinum–oxygen bond being broken, n_{CO} is the order of the carbon–oxygen bond initially present as a carbon monixide molecule, n_{Pt-Pt} is the free valence of the platinum surface, and n_{O-CO} is the order of the carbon–oxygen bond being formed as the carbon dioxide is synthesized. There are a total of five bonds which are conserved in the reaction.

There is no real justification for these bond conservation relationships in a complex rearrangement such as this. For simple hydrogen transfer reactions, bond conservation for an interaction of three electrons is at least plausible from a theoretical viewpoint, especially if the triplet repulsions are included. The extension to complex rearrangements in general and to surfaces in particular is without theoretical justification. Empirically it is probably best to view the bond conservation relations as a means of "keeping track" of the electrons involved in the chemical rearrangements.

It is convenient to present the calculated data in terms of a potential energy, V, defined by (energy units of kcal/mole)

$$V \equiv 349.2 - E, \qquad (3)$$

where E is given by

$$E = E_{Pt-O} + E_{CO_2}. \qquad (4)$$

In Eq. (4), $E_{Pt-O} = 46.6\, n_{Pt-O}$ since the single bond energy between platinum and oxygen is known to be 46.6 kcal/mole (*2,4*); and E_{CO_2} is the sum of the energy in both carbon–oxygen bonds of the carbon dioxide molecule being formed. The latter quantity may be found as a function of bond order from Fig. 4 and the Pauling relation for $n < 1.0$ (*11*). The quantity 349.2 kcal/mole in Eq. (3) comes from the fact the sum of the energy in a carbon–oxygen bond in carbon monoxide and in a platinum–oxygen bond on an e_g site is 349.2 kcal/mole ($2 \times 46.6 + 256$), i.e., the initial energy is shifted to a different zero.

A plot of potential energy of interaction, V, as a function of bond order between platinum and oxygen is shown in Fig. 5 where $0 \leq n_{Pt-O} \leq 2$. Carbon monoxide oxidation is exothermic by approximately 35 kcal/mole according to this Rideal–Eley mechanism, and there is an activation energy of approximately 16 kcal/mole. Before making further comments concerning carbon monoxide oxidation, it is necessary to consider a possible alternate mechanism.

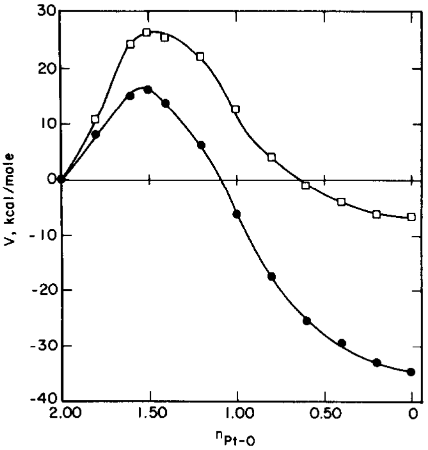

FIG. 5. Energetics of CO oxidation by O_2 on a Pt (111) surface. The Langmuir–Hinshelwood mechanism has an activation energy of 26 kcal/mole (□), and the Rideal–Eley mechanism has an activation energy of 16 kcal/mole (●).

Langmuir–Hinshelwood Mechanism

The Langmuir–Hinshelwood mechanism for the oxidation of carbon monoxide assumes that both the carbon monoxide and oxygen are adsorbed. In particular, the former is adsorbed molecularly on an e_g platinum (111) site, while the latter is adsorbed atomically on two e_g sites (*2*). The reaction may be written as

$$Pt{=}O(e_g\ \text{site}) + Pt{=}C{=}O(e_g\ \text{site}) \longrightarrow 2Pt + O{=}C{=}O(g), \qquad (5)$$

and on the left side of the equation there are double bonds between platinum and oxygen, platinum and carbon, and carbon and oxygen (*2*).

As in the Rideal–Eley mechanism, symmetric electron transfer is assumed from the platinum–oxygen double bond to the metal free valence and the carbon–oxygen bond being formed, and from the platinum–carbon double bond to the metal free valence and the carbon–oxygen bond being formed. The appropriate bond conservation relations are given by

$$\begin{aligned} n_{\mathrm{Pt-O}} &= 2 - n_{\mathrm{O-CO}}, \\ n_{\mathrm{Pt-CO}} &= 2 - n_{\mathrm{O-CO}}, \\ n_{\mathrm{CO_2}} &= 2 + n_{\mathrm{O-CO}}, \\ n_{\mathrm{Pt-Pt}} &= n_{\mathrm{O-CO}}, \end{aligned} \qquad (6)$$

where $0 \leqslant n_{\mathrm{O-CO}} \leqslant 2$. In Eq. (6), $n_{\mathrm{Pt-O}}$ is the bond order of the platinum–oxygen bond being broken, $n_{\mathrm{Pt-CO}}$ is the bond order of the platinum–carbon bond being broken, $n_{\mathrm{CO_2}}$ is the bond order of the carbon dioxide molecule being formed (i.e., two plus the bond order of the carbon–oxygen bond which is formed, $n_{\mathrm{O-CO}}$), and $n_{\mathrm{Pt-Pt}}$ is the free valence bond order of the platinum surface. There are a total of six bonds which are conserved.

The potential energy of the reaction which is chosen to represent the energetics of reaction is defined by (with energy in kcal/mole)

$$V \equiv 377.2 - E, \qquad (7)$$

where

$$E = E_{\mathrm{Pt-O}} + E_{\mathrm{Pt-CO}} + E_{\mathrm{CO_2}}. \qquad (8)$$

In Eq. (8), $E_{\mathrm{Pt-O}} = 46.6\ n_{\mathrm{Pt-O}}$ and $E_{\mathrm{Pt-CO}} = 46\ n_{\mathrm{Pt-CO}}$ since it is known that the single bond energies of platinum-oxygen and platinum-carbonyl bonds are 46.6 and 46 kcal/mole, respectively (*2*). The quantity $E_{\mathrm{CO_2}}$ is the sum of the energies in the two carbon–oxygen bonds in the product carbon dioxide molecule. This is given by 192 kcal/mole (for the carbon–oxygen double bond which is unperturbed throughout the reaction) plus the energy in the carbon–oxygen bond which is formed. This latter energy may be found as a function of bond order from Fig. 4. In Eq. (7), the quantity 377.2 kcal/mole is the total energy in the three reactant double bonds ($2 \times 46.6 + 2 \times 46 + 192$) and, as explained before, merely represents a shift of the energy zero.

The potential energy of interaction, V, for this Langmuir–Hinshelwood mechanism is shown in Fig. 5 as a function of bond order in the platinum–oxygen bond, $n_{\mathrm{Pt-O}}$. The reaction is exothermic by about 6.8 kcal/mole, and there is an activation energy of approximately 26 kcal/mole. This may be compared with the results of assuming a Rideal–Eley mechanism shown in Fig. 5. The difference in heats of reaction is clearly just the heat of adsorption of the carbon monoxide, i.e., 28 kcal/mole. More important is the difference in activation energies which favors the Rideal–Eley mechanism since it has an activation energy ca. 10.2 kcal/mole lower than that for the Langmuir–Hinshelwood mechanism.

These CFSO-BEBO model calculations for a platinum (111) surface agree qualitatively with the experimental results of Farnsworth on a nickel (100) surface (*12*). He observed no reaction between oxygen and carbon monoxide at room temperature, but carbon dioxide was observed to form when the nickel was heated to 525°K.

Bond (*13*) has reported on the oxidation of carbon monoxide over various forms of nickel, palladium, platinum and silver. For a palladium wire at 375°K, the activation energy for the reaction is 28.3 kcal/mole; while for palladium foil at 575°K, the activation energy is 22.2 kcal/mole. Over powdered silver at 375°K, the activation energy is 13.3 kcal/mole and on silver foil at 725°K, the activation energy is 13.3 kcal/mole. For powdered silver, the rate of oxidation is proportional to carbon monoxide pressure and is independent of oxygen pressure; whereas for silver foil, the rate is proportional to both carbon monoxide and oxygen pressure (*13*). No activation energies were reported for platinum or nickel, but they would not be expected to be greatly different from the palladium results. On palladium and platinum the reaction is reported to be first order in carbon monoxide and inhibited by oxygen (i.e., the reaction rate is inversely proportional to oxygen pressure). This is explicable in terms of the fact that carbon monoxide adsorption is unactivated on platinum, while oxygen chemisorption has a small activation energy. In the kinetic situation it is possible that the carbon monoxide adsorbs initially, and it is not replaced subsequently by the oxygen as the binding energies would suggest. Thus at surface temperatures below the desorption temperature of carbon monoxide (200–250°C), the carbon monoxide may compete with the oxygen for surface adsorption sites. Then the reaction on platinum would be expected to proceed via a Langmuir–Hinshelwood mechanism with an activation energy of ca. 26 kcal/mole rather than via a Rideal–Eley mechanism with an activation energy of only 16 kcal/mole. This Langmuir–Hinshelwood activation energy on platinum is in essential agreement with data cited above on palladium, and this mechanism also is consistent with the observed kinetics (*13*).

It has also been reported that when carbon monoxide and oxygen are exposed to either a nickel (100) or (110) surface at 310°K, a transient ir band due to $\mathrm{Ni}\cdots\mathrm{C}\underset{\cdots}{-}\mathrm{C}\underset{\cdots}{-}\mathrm{O}$ is observed, but carbon dioxide is not adsorbed on the nickel (*13*). This suggests that the reaction proceeds via a Rideal–Eley mechanism with gaseous carbon monoxide reacting with adsorbed oxygen. One expects this since the adsorption of oxygen on nickel is not activated (*2*), and the activation energies for the Langmuir–Hinshelwood and Rideal–Eley mechanisms for platinum (i.e., 26 and 16 kcal/mole, respectively) would be qualitatively correct for nickel also. Thus, the Rideal mechanism is favored, consistent with the experimental data cited above (*13*).

More recently in ultrahigh vacuum CO, oxidation has been studied on single crystals (*14–16*) on polycrystalline ribbons (*17*) and on epitaxial films using molecular beam techniques (*18*). In this work the reaction probabilities for the Rideal–Eley reaction are nearly unity and show little if any temperature dependence. Therefore the calculated activation energy of 16 kcal is much too high. At low temperatures these investigators (*14–18*) have found that CO adsorbs on the surface and hinders O_2 adsorption because the sticking coefficient for CO is larger than it is for O_2.

The activation energies for the Langmuir–Hinshelwood reaction is much larger, ca. 37 kcal/mole (*19*), but of course the preexponential is much greater for this reaction than for the Rideal–Eley case at low pressures. At high pressures, e.g., 1 atm, the impingement rates are fast enough that the Rideal–Eley is clearly the main reaction channel. Nevertheless, the Langmuir–Hinshelwood reaction still plays a major role in reaction "light-off" from a low temperature where the surface is initially poisoned with adsorbed CO. It accelerates the clean-off reaction to generate active surface for the Rideal–Eley reaction.

These elementary reactions are very rapid, i.e., O_2 adsorption has sticking coefficients at least as high as 10^{-2} and Rideal–Eley reaction probabilities are near unity. As a result conventional porous catalysts usually operate within the diffusion controlled regime. This tends to favor the Langmuir–Hinshelwood reaction, especially at low CO concentrations and the high activation energies quoted earlier may have resulted from transport limited reaction conditions, which favor a Langmuir–Hinshelwood channel for the reaction.

The ultrahigh vacuum studies make it clear that the CFSO-BEBO calculations have calculated activation energies much too large for the Rideal–Eley mechanism, though the semiqualitative prediction that the surface–surface reaction has a substantially larger activation energy than the gas–surface reaction is correct.

Reduction of Nitric Oxide on Platinum (111)

Rideal–Eley Mechanism

The reduction of nitric oxide by carbon monoxide can be examined in a manner similar to that for the oxidation of carbon monoxide by oxygen which was discussed above. Using the CFSO-BEBO model the heat of adsorption of molecular nitric oxide on a platinum (111) e_g site has been calculated to be 25 kcal/mole (*20*), and the heat of adsorption of molecular carbon monoxide on an e_g site on the platinum surface is 28 kcal/mole (*2*). The interaction energy between a nitric oxide molecule and an e_g site of a platinum (111) surface is shown as a function of bond order in Fig. 6 (*20*). It is thus expected that nitric oxide and carbon monoxide would adsorb competitively on platinum, and it has been reported that nitric oxide can compete with carbon monoxide in the adsorbed phase on a nickel (100) surface (*14*). In formulating the Rideal–Eley mechanism, it will be assumed that the nitric oxide is adsorbed on the platinum (111) surface and the carbon monoxide interacts with it from the gas phase. This is the preferred mechanism from a stoichiometric point of view when one considers that carbon monoxide is adsorbed as a carbonyl and that gaseous carbon monoxide is a linear oxygen–carbon–oxygen molecule. The reaction product is a carbon dioxide molecule in the gas phase and a nitrogen atom which remains on the metal surface. The reaction is written as

$$\text{Pt—NO}(e_g \text{ site}) + \text{C}{\equiv}\text{O(g)} \longrightarrow \text{Pt}{\equiv}\text{N} + \text{O}{=}\text{C}{=}\text{O(g)} \quad (9)$$

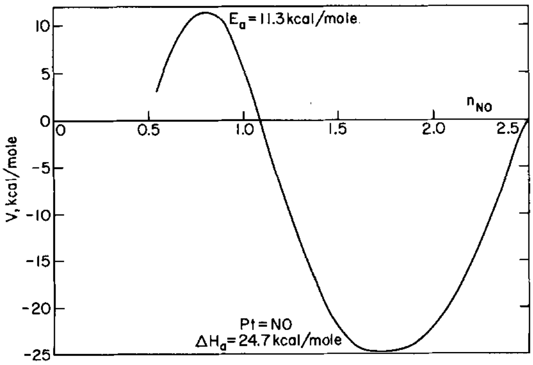

FIG. 6. Interaction energy between NO molecule and an e_g site of a Pt (111) surface as a function of bond order with $E_{\text{Pt-NO,s}} = 32$ kcal/mole and $E_{\text{Pt-O,s}} = 46.6$ kcal/mole. Initial interaction is through the nitrogen atom.

It may be seen from Fig. 6 that a nitric oxide molecule adsorbed on an e_g site has a platinum–nitrogen bond order of 1.56 and a nitrogen–oxygen bond order of 1.72. The bond conservation relations for the reaction of Eq. (9) analogous to Eq. (2) for the reaction of Eq. (1) are given by

$$\begin{aligned} n_{\text{Pt-NO}} &= 1.56 + 0.72\, n_{\text{O-CO}}, \\ n_{\text{NO}} &= 1.72 - 0.86\, n_{\text{O-CO}}, \\ n_{\text{CO}} &= 3 - 0.50\, n_{\text{O-CO}}, \\ n_{\text{Pt-Pt}} &= 0.72 - 0.36\, n_{\text{O-CO}}, \end{aligned} \quad (10)$$

where $0 \leqslant n_{\text{O-CO}} \leqslant 2$. In Eq. (10), $n_{\text{Pt-NO}}$ is the bond order in the platinum–nitrogen bond which increases from 1.56 to 3.00, n_{NO} is the bond order in the nitrogen–oxygen bond which is broken, n_{CO} is the bond order in the carbon–oxygen bond which decreases from 3.00 to 2.00, $n_{\text{Pt-Pt}}$ is the platinum free valence which decreases from 0.76 to 0, and $n_{\text{O-CO}}$ is the bond order of the carbon–oxygen bond being formed which increases from 0 to 2.00. There are a total of seven bonds conserved in the reaction.

The potential energy of interaction for reaction (9) is defined by (with energy units of kcal/mole)

$$V \equiv 432 - E, \quad (11)$$

where E is given by

$$E = E_{\text{Pt-NO}} + E_{\text{CO}_2}. \quad (12)$$

In Eq. (12), $E_{\text{Pt-NO}} = 32\, n_{\text{Pt-NO}}$ (*14*), the single order bond energy for a platinum–nitrogen bond is 40 kcal/mole (*14*), and E_{CO_2} is the sum of the energy in both

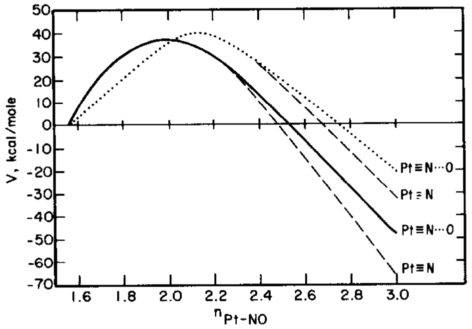

FIG. 7. Energetics of NO reduction by CO on a Pt (111) surface. The Langmuir–Hinshelwood mechanism has an activation energy of 40 kcal/mole (···), and the Rideal–Eley mechanism has an activation energy of 38 kcal/mole (—); (---) a final state with $E_{Pt-N} = 40$ kcal/mole instead of 32 kcal/mole.

carbon–oxygen bonds and may be obtained as a function of bond order from Fig. 4. The quantity 432 kcal/mole in Eq. (11) corresponds to the summation of the energy in the 1.56 order Pt–NO bond (50 kcal/mole), in the 1.72 order nitrogen–oxygen bond (126 kcal/mole), and in the unperturbed carbon monoxide molecule (256 kcal/mole), i.e., in the reactants. As before, this corresponds to a shift in the zero of potential energy.

This potential energy of interaction is plotted in Fig. 7 as a function of platinum–nitrogen bond order ($1.56 \leq n_{Pt-N} \leq 3.00$). The calculation has used 32 kcal for the single bond energy of Pt–NO, but as the NO bond order approaches zero the platinum–nitrogen bonding should be more like that of Pt–N, whose bond energy is 40 kcal/mole. This is illustrated schematically in Fig. 7 with the broken line. The Rideal–Eley mechanism is exothermic by 67 kcal/mole, and there is an activation energy of 37 kcal/mole.

Langmuir–Hinshelwood Mechanism

The Langmuir–Hinshelwood mechanism for the reduction of nitric oxide by carbon monoxide involves the breaking of the nitrogen–oxygen bond of the nitric oxide molecule adsorbed at a platinum (111) e_g site ($n_{NO} = 1.72$, $n_{Pt-NO} = 1.56$) with the oxygen atom beginning to bond to the carbon atom of the carbon monoxide adsorbed initially at an adjacent e_g site ($n_{CO} = n_{Pt-CO} = 2.00$). This reaction may be written as

$$\begin{aligned} &\text{Pt—NO}(e_g\text{ site}) + \text{Pt}{=}\text{CO}(e_g\text{ site}) \longrightarrow \\ &\quad \text{Pt} + \text{Pt}{\equiv}\text{N}(e_g\text{ site}) + \text{O}{=}\text{C}{=}\text{O(g)} \end{aligned} \tag{13}$$

In analogy to the Langmuir–Hinshelwood mechanism for the oxidation of carbon monoxide by oxygen as given by Eq. (5) above, the bond conservation equations applicable to Eq. (13) are given by

$$\begin{aligned} n_{Pt-NO} &= 1.56 + 0.72\, n_{O-CO}, \\ n_{Pt-CO} &= 2.00 - n_{O-CO}, \\ n_{NO} &= 1.72 - 0.86\, n_{O-CO}, \\ n_{CO_2} &= 2 + n_{O-CO}, \\ n_{Pt-Pt} &= 0.72 + 0.36\, n_{O-CO}, \end{aligned} \tag{14}$$

where $0 \leq n_{O-CO} \leq 2$. The bond orders n_{Pt-NO}, n_{NO}, n_{O-CO} and n_{Pt-Pt} were defined below Eq. (10), n_{Pt-CO} is the platinum–carbonyl bond order of the bond being broken which decreases from 2 to 0, and n_{CO_2} is the bond order in the carbon dioxide molecule being formed (i.e., two plus the order of the carbon–oxygen bond which is formed). There are a total of eight bonds conserved according to this reaction mechanism.

The potential energy of this reaction, shifted as before so that the reactants have zero potential, is given (kcal/mole) by

$$V = 460 - E, \tag{15}$$

where E is given by

$$E = E_{Pt-NO} + E_{Pt-CO} + E_{NO} + E_{O-CO} + 192. \tag{16}$$

In Eq. (16), $E_{Pt-NO} = 32\, n_{Pt-NO}$ where 32 kcal/mole is the single order bond energy for a platinum–nitrogen bond, $E_{Pt-CO} = 46\, n_{Pt-CO}$ where 46 kcal/mole is the single order bond energy for a platinum–carbonyl bond, E_{NO} and E_{O-CO} are the bond energies in the nitrogen–oxygen and carbon–oxygen bonds, respectively, obtained as a function of bond order from Fig. 4. The quantity 192 is the bond energy of the C=O which is unchanged during the reaction. As noted above Eq. (15), E for the reactants is 460 kcal/mole $(50 + 92 + 126 + 192)$.

The potential energy of interaction, V, is plotted in Fig. 7 as a function of bond order in the platinum–nitrogen bond according to this Langmuir–Hinshelwood mechanism. The reaction is exothermic by 33 kcal/mole, and there is an activation energy of 40 kcal/mole. The difference in exothermicities of the two reaction mechanisms is just the heat of adsorption of carbon monoxide on platinum (111), 28 kcal/mole. Since the activation energies of these two mechanisms are so similar, i.e., 37 vs 40, niether can be eliminated a priori. However, from Fig. 6 it is seen that the activation energy for dissociation of the nitric oxide molecule on the platinum surface is only 12 kcal/mole, which is substantially less than the activation energy for either of the reaction mechanisms. Thus, the CFSO-BEBO model predicts that the reduction of nitric oxide by carbon monoxide would proceed in the following way:

1. The nitric oxide molecule dissociates on the platinum (111) surface with an activation energy of 12 kcal/mole.
2. The carbon monoxide reacts with the adoxygen atom according to the Rideal–Eley mechanism to form carbon dioxide in the gas phase with an activation energy of 16 kcal/mole. (This reaction was discussed in detail in Sect. A above.)
3. The platinum surface is regenerated by N_2 desorption at high temperatures or by a reaction with other nitric oxide molecules to form a nitrous oxide molecule at low temperatures.

Shelef and Otto (*22*) have studied the reduction of nitric oxide by carbon monoxide over a platinum catalyst on a 95% alumina–5% silica support. The reaction was studied in an integral flow reactor, and the products were analyzed mass spectrometrically. It was found that carbon dioxide is formed as the carbon monoxide is oxidized by the nitric oxide, but that the other reaction product is nitrous oxide rather than nitrogen at a lower surface temperature. The nitrous oxide reaction product reaches a maximum concentration at 575°K, below which temperature essentially no nitrogen is formed. As the surface temperature is increased, the nitrous oxide concentration decreases, while the nitrogen concentration increases. This is in agreement with the CFSO-BEBO model predictions, i.e., the activation energy for nitrogen to be desorbed except at high surface temperatures. The CFSO-BEBO nitrogen to be desorbed except at high surface temperatures. The CFSO-BEBO model has also been used to examine the reaction of nitric oxide with adsorbed nitrogen (Langmuir–Hinshelwood and Rideal–Eley kinetics). The activation energy for the Rideal–Eley, which is more favorable, is 21 kcal/mole (*23*), substantially less than that required for desorption of N_2 (*3*).

Lambert and Comrie (*23*) have examined simultaneous adsorption of CO and NO on Pt (111) and Pt (110). In agreement with the CFSO-BEBO calculations they found that CO displaces NO, that NO adsorbs associatively, and that the surface reaction of CO and NO proceeds by NO dissociation followed by reaction of adsorbed oxygen with CO and the thermal desorption of N_2. The calculations are also in qualitative agreement with results on supported catalysts (*24,25*). Shelef *et al.* (*26*) studied the oxidation of CO by O_2 and NO simultaneously. The O_2 rate is more rapid than the NO rate. In both cases, according to the calculations presented, the oxygen atom is removed via the same reaction, i.e., $O + CO \rightarrow CO_{2g}$ which is (empirically) a fast reaction. The relative rates should scale then according to the rate of formation of the adsorbed O atom. The CFSO-BEBO calculations give 2–4 kcal/mole for dissociative O_2 adsorption (*2*) and 12 kcal/mole for dissociative NO adsorption, which is in qualitative agreement with the relative rate measurements (*26*).

Water Synthesis Reaction on Platinum (111)

Rideal–Eley Mechanism

The hydrogen reaction with oxygen on platinum (111) to form water can be analyzed according to the Rideal–Eley mechanism just as has been done for the two carbon monoxide oxidation reactions above. Oxygen adsorbs much more strongly than hydrogen on platinum (*1*,*2*) so the reaction will be assumed to occur via the interaction of an adoxygen atom at an e_g site and molecular hydrogen in the gas phase. This reaction is written as

$$\mathrm{Pt{=}O}(e_g\ \text{site}) + \mathrm{H_2(g)} \longrightarrow \mathrm{Pt + H{-}O{-}H(g)}. \quad (17)$$

The appropriate bond conservation relations are given by

$$\begin{aligned} n_{\mathrm{Pt-O}} &= 2 - 2\, n_{\mathrm{O-H}}, \\ n_{\mathrm{H-H}} &= 1 - n_{\mathrm{O-H}}, \\ n_{\mathrm{H_2O}} &= 2\, n_{\mathrm{O-H}}, \\ n_{\mathrm{Pt-Pt}} &= n_{\mathrm{O-H}}, \end{aligned} \quad (18)$$

where $0 \leqslant n_{\mathrm{O-H}} \leqslant 1$. In Eq. (18), the platinum–oxygen bond order, $n_{\mathrm{Pt-O}}$, decreases from 2 to 0 during the reaction; the hydrogen-hydrogen bond order $n_{\mathrm{H-H}}$, decreases from 1 to 0; the platinum free valence $n_{\mathrm{Pt-Pt}}$, increases from 0 to 1; and the hydrogen–oxygen bond order, $n_{\mathrm{O-H}}$, increases from 0 to 1 with two of these bonds being formed simultaneously. There are a total of three bonds being formed simultaneously. There are a total of three bonds which are conserved.

The potential energy of the reaction is defined by (kcal/mole.

$$V \equiv 196.4 - E, \quad (19)$$

where

$$E = E_{\mathrm{Pt-O}} + E_{\mathrm{H_2}} + E_{\mathrm{H_2O}}. \quad (20)$$

In Eq. (20), $E_{\mathrm{Pt-O}} = 46.6\, n_{\mathrm{Pt-O}}$ since the single order bond energy for a platinum–oxygen bond is 46.6 kcal/mole; and $E_{\mathrm{H_2}}$ and $E_{\mathrm{H_2O}}$ are the bond energies in the hydrogen and water molecules, respectively. The former is given by (*11*)

$$E_{\mathrm{H_2}} = 103.2\, (n_{\mathrm{H_2}})^{1.041}; \quad (21)$$

while the latter is given by (*10*)

$$E_{\mathrm{H_2O}} = 218.8\, (n_{\mathrm{O-H}})^{1.028}. \quad (22)$$

The quantity 196.4 kcal/mole in Eq. (19) is the energy in the reactant bonds, i.e., 103.2 kcal/mole in the hydrogen molecule and $2 \times 46.6 = 93.2$ kcal/mole in the platinum–oxygen bond; and as before the zero of energy for the reactants has merely been shifted by that amount.

The potential energy, V, is plotted in Fig. 8 as a function of total bond order in the water molecule formed in the reaction,

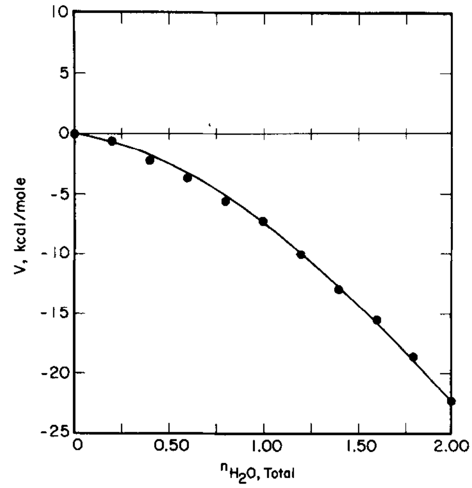

FIG. 8. Energetics of the reaction of H_2 with O_2 on a Pt (111) surface. The Rideal–Eley mechanism is unactivated, whereas the Langmuir–Hinshelwood mechanism is not only activated but also endothermic.

i.e., 2 n_{O-H}. The reaction according to the Rideal–Eley mechanism is unactivated and exothermic by ca. 22 kcal/mole. This result is in agreement with the experimental results of Tucker (*27*) on a platinum (111) surface. He found that when a platinum (111) surface with a (2 × 2) oxygen overlayer was exposed at room temperature to hydrogen there was an *immediate* removal of the oxygen structure indicating a reaction between the hydrogen and oxygen to form water. The fact that the oxygen structure was immediately removed at room temperature indicates the reaction is unactivated in agreement with the theoretical results of the CFSO-BEBO model.

Smith and Palmer (*28*) have impinged a thermal beam of deuterium molecules onto an oxygen covered platinum (111) surface and have detected deuterated water as a reaction product in the scattered beam. The reaction probability is very high and the apparent activation energy based on the deuterium temperature was only a few kilocalories per mole. These results have been confirmed by Bernasek and Somorjai (*29*). Ducros and Merrill and Stoll and Merrill (*16*) have observed reaction probabilities of ca. unity for the removal of atomically adsorbed oxygen from platinum (110) and (111) surfaces. May and Germer (*30*) have also found a relatively high reaction probability for the hydrogen reaction with oxygen adsorbed on a nickel (110) surface.

Bond (*13*) has reported that Group VIII and IB metals are the most efficient catalysts for the oxidation of hydrogen. Both platinum and palladium catalyze the reaction at room temperature, and over various platinum catalysts the rate of formation of water is proportional to hydrogen pressure and independent of oxygen pressure. This observation is in accord with the Rideal–Eley mechanism presented above.

Langmuir–Hinshelwood Mechanism

The Langmuir–Hinshelwood mechanism for the hydrogen–oxygen reaction on platinum to form water may be written as

$$\mathrm{Pt{=}O}(e_g\ \text{site}) + 2\ \mathrm{Pt{-}H}(e_g\ \text{site}) \longrightarrow 3\ \mathrm{Pt} + \mathrm{H_2O(g)}. \quad (23)$$

This mechanism need not be studied in detail since it is readily apparent that it is endothermic as written. In fact, the heat of reaction is +8.4 kcal/mole (2 × 46.6 + 2 × 67 − 2 × 109.4) since the platinum–hydrogen single order bond energy is 67 kcal/mole (*1*). Thus, on the basis of energetics, the Langmuir–Hinshelwood mechanism for the water synthesis reaction on platinum may immediately be rejected in favor of the Rideal–Eley mechanism discussed in detail above.

SUMMARY

The empirical CFSO-BEBO model, discussed in detail previously for chemisorption on platinum and nickel surfaces (*1–4*), has been applied to several surface reactions on platinum in the present paper. The results for the reactions of carbon monoxide and oxygen, carbon monoxide and nitric oxide, and hydrogen and oxygen were presented, discussed, and compared with experimental data in Sect. II. The results are summarized in Table 1 with the reaction mechanism (either Rideal–Eley or Langmuir–Hinshelwood), and the corresponding activation energies to reaction given. All three reactions are predicted to proceed via the Rideal–Eley mechanism at moderately high pressures. At very low pressures the Langmuir–Hinshelwood mechanism may predominate because the preexponential term in the surface–surface reaction can be much greater than the product of the preexponential and the impingement rate for gas–surface reaction. The nitric oxide and carbon monoxide reaction is interesting because it is predicted that the adsorbed nitric oxide molecule will dissociate on the platinum surface prior to reaction, and the carbon monoxide will react with the adsorbed oxygen atom just as in the carbon monoxide and oxygen reaction.

TABLE 1
Summary of Calculated Results for Platinum Catalyzed Surface Reactions

Reaction	Mechanism	E_a (kcal/mole)
1. O_2 + CO	Rideal–Eley	17
	Langmuir–Hinshelwood	27
2. NO + CO	Rideal–Eley	37
	Langmuir–Hinshelwood	40
3. H_2 + O_2	Rideal–Eley	0
	Langmuir–Hinshelwood	Endothermic by 8.4

In order to treat surface reactions from a theoretical point of view, it is necessary to have a reliable theory of chemisorption. It has been pointed out that such an *ab initio* theory of chemisorption is not now available, nor is it likely to be available in the near future (*1–3*). In the meanwhile, an empirical model of chemisorption such as the CFSO-BEBO model should prove valuable. In this paper the usefulness of the CFSO-BEBO model has been extended by applying it to heterogeneously catalyzed surface reactions. In addition to predicting activation energies to reaction, the model can establish the most energetically favorable mechanism for reaction from among a set of reasonable alternatives, e.g., the model can predict whether a Langmuir–Hinshelwood or a Rideal–Eley mechanism should be expected for some simple surface reactions. A final impressive feature of the model is its extreme simplicity. In a future publication the CFSO-BEBO model will be used to extend the treatment of the adsorption of ethylene and hydrogen (*31*) to ethylene hydrogenation.

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